UNITED STATES PATENT APPLICATION

OF

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AND

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FOR

TANTALUM AMIDE PRECURSORS FOR DEPOSITION OF TANTALUM NITRIDE ON A SUBSTRATE

INTELLECTUAL PROPERTY/TECHNOLOGY LAW
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BACKGROUND OF THE INVENTION

Field Of The Invention

The present invention relates to Ta and Ti precursors useful in the formation of a Ta-based or Ti-based material on a substrate, and includes tantalum amide precursors for formation of tantalum nitride on a substrate, and methods of use of such precursors for forming TaN material, e.g., thin film layers of TaN, on a substrate. The invention also contemplates single source compounds for the formation of TaSiN or TiSiN material on a substrate.

Description of the Related Art

Copper is of great interest for use in metallization of VLSI microelectronic devices because of its low resistivity, low contact resistance, and ability to enhance device performance (relative to aluminum metallization) via reduction of RC time delays thereby producing faster microelectronic devices. Copper CVD processes which are suitable for large-scale manufacturing and the conformal filling of high aspect ratio inter-level vias in high density integrated circuits are extremely valuable to the electronics industry, and are therefore being extensively investigated in the art.

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Although CVD of Cu is gaining momentum in the semiconductor manufacturing industry, several problems still inhibit the integration of copper metallurgy in such microelectronic device applications. In specific, CVD of a suitable diffusion barrier for the copper metallization must be available to ensure the long-term reliability of the copper-based metallurgy in integrated circuits (ICs).

TaN and TaSiN have been demonstrated as a suitable metal diffusion barrier. A CVD process of TaN would obviously be advantageous and is currently the focus of development efforts by semiconductor equipment manufacturers. The CVD of TaN is at present carried out using $Ta(NMe_2)_5$, a solid source precursor, as the source reagent. However, $Ta(NMe_2)_5$ is a solid, and given the limited volatility of $Ta(NMe_2)_5$, new, robust and more volatile tantalum amide precursors are needed. The films deposited from such sources must be conducting, conformal and of high purity. It would be extremely advantageous to utilize a suitable liquid source reagent as a tantalum amide precursor. For example, an alternative TaN precursor is $Ta(NEt_2)_5$, which is reportedly a liquid. However, this source reagent is unstable to elevated temperature conditions, readily decomposing to a tantalum imide species, $Ta(NEt)(NEt_2)_3$, upon heating, and thereby is an unsatisfactory candidate as a liquid source reagent for TaN barrier layer formation.

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TaSiN and TiSiN are also currently being investigated in the art as diffusion barriers. A CVD process for these ternary barrier layer materials would also be advantageous and also is the focus of development efforts in the field. The CVD of TaSiN is at present carried out using $Ta(NMe_2)_5$ as the Ta source and silane as the silicon source. Further, $TaCl_5$ in combination with silane and ammonia has been used to deposit TaSiN thin films. Apart from the hazards associated with handling a pyrophoric gas such as silane, the dual source reactor configuration required with such precursor species ($TaCl_5$, $Ta(NMe_2)_5$ and silane) also increases the cost and complexity of the semiconductor manufacturing operation.

Another approach to barrier layer formation entails the PVD or CVD deposition of high purity Ta metal on the silicon substrate. The resulting Ta layer will form $TaSi_x$ at the silicon contact region (i.e., the Ta bottom surface), and subsequent elevated temperature reaction of the Ta layer with a nitrogenous reactant such as NH_3 or N_2 will induce nitridation of the Ta top-surface. Thus, a TaSiN ternary diffusion barrier or a layered TaSi / TaN structure can be formed. This type of ternary diffusion barrier has been reported in the art and provides excellent contact resistance and diffusion barrier properties towards Cu metallization and integration of ferroelectric thin films.

In all instances of the formation of a Ta-based diffusion barrier, an effective CVD approach to conformally coat inter-level (< 0.15 μm) vias and sidewalls is critical, and the

CVD source reagent must be storage-stable, of appropriate volatility and vaporization characteristics, with good transport and deposition characteristics to produce a high-purity, electronic quality thin film.

There is a continuing and increasing need in the art for improved CVD source reagents for forming Ta-based diffusion barrier layers on microelectronic substrates, to facilitate copper metallization. Such CVD source reagents are desirably liquid in character, to facilitate their processibility using techniques such as liquid delivery CVD, wherein the liquid source reagent is rapidly vaporized, e.g., by flash vaporization on a heated element such as a grid, screen or porous metal body, to produce a volatilized source reagent. The resulting source reagent vapor can then be transported to the CVD chamber and contacted with a substrate maintained at appropriate elevated temperature, to effect the deposition on the substrate of the Ta-based material.

It therefore is an object of the present invention to provide useful precursor compositions for the formation of Ta-based material and Ti-based material on substrates.

It is another object of the invention to provide a method of forming a Ta-based material, such as TaN or TaSiN, or a Ti-based material, such as TiN or TiSiN, on a substrate, using such precursor compositions.

Other objects and advantages of the present invention will be more fully apparent from the ensuing disclosure and appended claims.

SUMMARY OF THE INVENTION

The present invention relates generally to tantalum and titanium source reagents for the formation of Ta-based and Ti-based materials on a substrate by techniques such as chemical vapor deposition, and in particular and preferred practice of the invention, liquid delivery chemical vapor deposition.

As used herein, the term "liquid delivery" when referred to chemical vapor deposition or other thin film or coating process refers to the fact that the precursor or source reagent composition for the material to be deposited on a substrate is vaporized from a liquid form to produce a corresponding precursor vapor which then is transported to the locus of deposition, to form the material film or coating on the substrate structure. The liquid phase which is vaporized to form the precursor vapor may comprise a liquid-phase source reagent per se, or the source reagent may be dissolved in or mixed with a liquid to facilitate such vaporization to place the source reagent in the vapor phase for the deposition operation.

As used herein, the term "perfluoroalkyl" is intended to be broadly construed to include groups containing alkyl moieties which are partially or fully substituted in

fluorine atoms, and thus perfluoroalkyl includes for example a trifluoroalkyl substituent whose alkyl moiety is C_1-C_4 alkyl, such as trifluoromethyl.

In one compositional aspect, the present invention relates to a precursor composition comprising at least one tantalum and/or titanium species selected from the group consisting of:

(i) tethered amine tantalum complexes of the formula:

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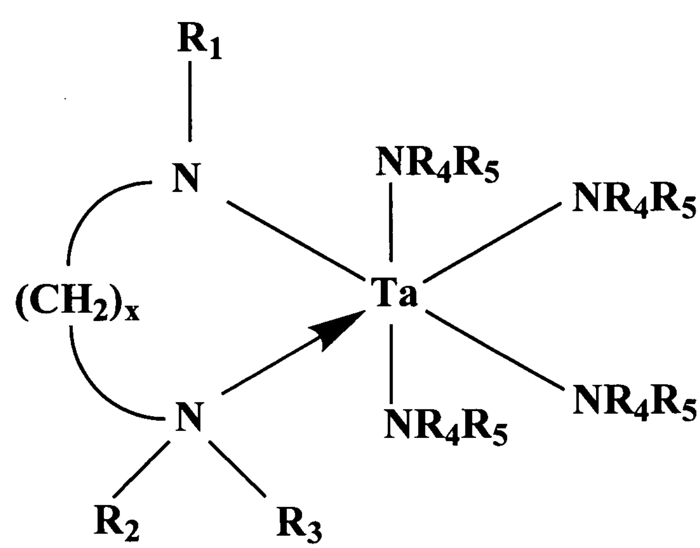

wherein:

X is 2 or 3;

each of R_1-R_5 is independently selected from the group consisting of H, C_1-C_4 alkyl, aryl (e.g, phenyl), C_1-C_6 perfluoroalkyl (e.g., a trifluoroalkyl substituent whose alkyl moiety is C_1-C_4 alkyl, such as trifluoromethyl), and trimethylsilyl;

(ii) β-diimines of the formula:

$$TaG_xQ_{5-x}$$

wherein:

G is a β-diimino ligand;

each Q is selected from the group consisting of H, C_1-C_6 alkyl, aryl and C_1.C_6 perfluoroalkyl; and

x is an integer from 1 to 4 inclusive;

(iii) tantalum diamide complexes of the formula

$$Ta(N(R_1)(CH_2)_xN(R_2))_y(NR_3R_4)_{5-2y}$$

wherein:

x is 1 or 2;

y is 1 or 2;

each of R_1-R_4 is independently selected from the group consisting of H, C_1-C_4 alkyl, aryl, perfluoroalkyl, and trimethylsilyl;

(iv) tantalum amide compounds of the formula

$$Ta(NRR')_5$$

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wherein each R and R' is independently selected from the group consisting of H, C_1-C_4 alkyl, phenyl, perfluoroalkyl, and trimethylsilyl, subject to the proviso that in each NRR' group, $R \neq R'$;

(v) β-ketoimines of the formula

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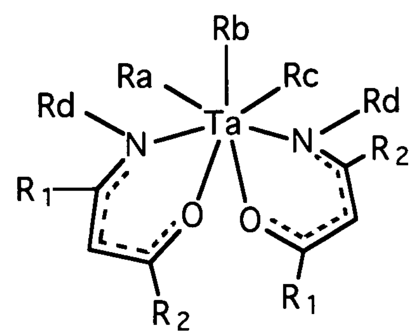

wherein each of R_1, R_2, R_a, R_b, R_c and R_d is independently selected from H, aryl, C_1-C_6 alkyl, and C_1-C_6 perfluoroalkyl; and

(v) tantalum cyclopentadienyl compounds of the formula:

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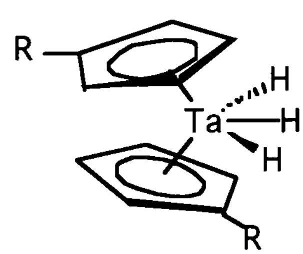

wherein each R is independently selected from the group consisting of H, methyl, ethyl, isopropyl, t-butyl, trimethylsilyl;

(vii) $Ta(NR_1R_2)_x(NR_3R_4)_{5-x}$ / $Ti(NR_1R_2)_x(NR_3R_4)_{4-x}$

or $Ta(NR_1)(NR_2R_3)_3$

where each of R_1, R_2, R_3 and R_4 are independently selected from the group consisting of H, C_1-C_8 alkyl (e.g., Me, Et, ^{t}Bu, ^{i}Pr, etc.), aryl (e.g., phenyl), C_1-C_8 perfluoroalkyl (e.g., CF_3 or a fluoroalkyl whose alkyl moiety is C_1-C_4, such as trifluoromethyl), or a silicon-containing group such as silane (SiH_3), alkylsilane, (e.g., $SiMe_3$, $Si(Et)_3$, $Si(^iPr)_3$, $Si(^tBu)_3$, perfluoroalkylsilyl (e.g., $Si(CF_3)_3$), triarylsilane (e.g,, $Si(Ph)_3$), or alkylsilylsilane (e.g., $Si(SiMe_3)_x(Me)_{3-x}$);

(viii) $Ta(SiR_1R_2R_3)_x(NR_4R_5)_{5-x}$ / $Ti(SiR_1R_2R_3)_x(NR_4R_5)_{4-x}$

where R_{1-5} can any be combination of H, Me, Et, ^{t}Bu, Ph, ^{i}Pr, CF_3, SiH_3, $SiMe_3$, $Si(CF_3)_3$, $Si(Et)_3$, $Si(^iPr)_3$, $Si(^tBu)_3$, $Si(Ph)_3$, and $Si(SiMe_3)_x(Me)_{3-x}$; and

(ix) $(Cp^n)Ta(SiR_1R_2R_3)_x(NR_4R_5)_{4-x}$ / $(Cp^n)_2Ti(SiR_1R_2R_3)(NR_4R_5)$

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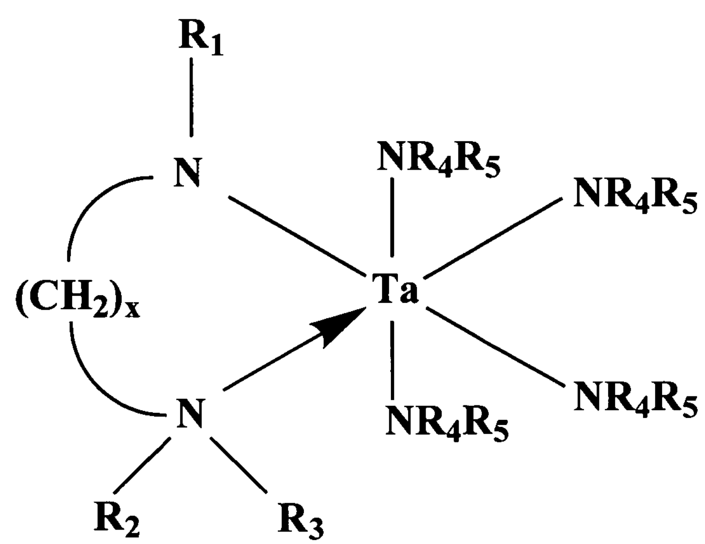
where R_{1-5} can any be combination of H, Me, Et, ^tBu, Ph, ^iPr, CF_3, SiH_3, $SiMe_3$, $Si(CF_3)_3$, $Si(Et)_3$, $Si(^iPr)_3$, $Si(^tBu)_3$, $Si(Ph)_3$, $Si(SiMe_3)_x(Me)_{3-x}$ and Cp^n is $C_5H_xMe_{(5-x)}$ (where x = 0-5).

In one aspect, the present invention relates to tantalum amide precursors for formation of tantalum nitride on a substrate, and to methods of forming TaN material on a substrate from such precursors, wherein the precursor composition comprises at least one tantalum species selected from the group consisting of:

(i) tethered amine tantalum complexes of the formula:



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wherein:

X is 2 or 3;

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each of R_1-R_5 is independently selected from the group consisting of H, C_1-C_4 alkyl, aryl (e.g, phenyl), C_1-C_6 perfluoroalkyl (e.g., a trifluoroalkyl substituent whose alkyl moiety is C_1-C_4 alkyl, such as trifluoromethyl), and trimethylsilyl;

(ii) β-diimines of the formula:

$$TaG_xQ_{5-x}$$

wherein:

G is a β-diimino ligand;

each Q is selected from the group consisting of H, C_1-C_6 alkyl, aryl and C_1-C_6 perfluoroalkyl; and

x is an integer from 1 to 4 inclusive;

(iii) tantalum diamide complexes of the formula

$$Ta(N(R_1)(CH_2)_xN(R_2))_y(NR_3R_4)_{5-2y}$$

wherein:

x is 1 or 2;

y is 1 or 2;

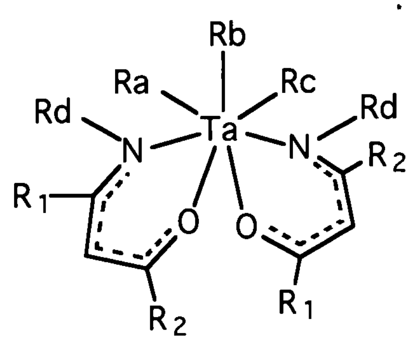
each of R_1-R_{-4} is independently selected from the group consisting of H, C_1-C_4 alkyl, aryl, perfluoroalkyl, and trimethylsilyl;

(iv) tantalum amide compounds of the formula

$$Ta(NRR')_5$$

wherein each R and R' is independently selected from the group consisting of H, C_1-C_4 alkyl, phenyl, perfluoroalkyl, and trimethylsilyl, subject to the proviso that in each NRR' group, $R \neq R'$;

(v) β-ketoimines of the formula



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wherein each of R_1, R_2, R_a, R_b, R_c and R_d is independently selected from H, aryl, C_1-C_6 alkyl, and C_1-C_6 perfluoroalkyl; and

(vi) tantalum cyclopentadienyl compounds of the formula

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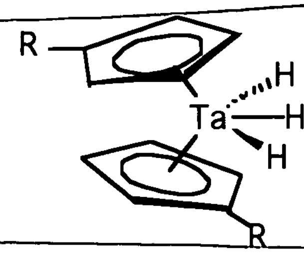

wherein each R is independently selected from the group consisting of H, methyl, ethyl, isopropyl, t-butyl, trimethylsilyl.

In another aspect, the present invention relates to a tantalum amide precursor composition for forming a tantalum nitride material on a substrate, including at least one tantalum amide species selected from the above-described selection group, and a solvent for such tantalum amide species. The solvent may be selected from the group consisting of C_6-C_{10} alkanes, C_6-C_{10} aromatics, and compatible mixtures thereof. Illustrative alkane species include hexane, heptane, octane, nonane and decane. Preferred alkane solvent species include C_8 and C_{10} alkanes. Preferred aromatic solvent species include toluene and xylene. In the most preferred approach, no solvent is required to deliver the liquid source reagents.

In another aspect, the invention relates to a method of forming a tantalum nitride material on a substrate from a precursor composition therefor, including the steps of vaporizing the precursor composition to form a precursor vapor and contacting the precursor vapor with a substrate under deposition conditions to deposit on the substrate the tantalum nitride material, wherein the tantalum nitride precursor composition

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comprises at least one tantalum amide species selected from the above-described selection group of tantalum compounds and complexes, in a solvent for the tantalum amide species.

The tantalum nitride precursor composition thus may be provided as a liquid composition, which is delivered to a vaporizer to effect vaporization and formation of the tantalum nitride precursor vapor, with the vapor being transported to a deposition zone containing the substrate for the formation of the tantalum nitride material on the substrate. The formation of tantalum nitride material on the substrate may be carried out by a deposition process such as chemical vapor deposition, assisted chemical vapor deposition, ion implantation, molecular beam epitaxy and rapid thermal processing.

Other aspects and features of the invention will be more fully apparent from the ensuing disclosure and appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a Thermal Gravimetric Analysis (TGA) plot comparing the volatility of $Ta(NMeEt)_5$ with $Ta(NEt)(NEt_2)_3$ and $Ta(NMe)_5$.

Figure 2 is an STA plot of $Ta(NMeEt)_5$.

Figure 3 is a ^{1}H and ^{13}C NMR plot for $Ta(NMeEt)_5$ showing five equivalent amide groups.

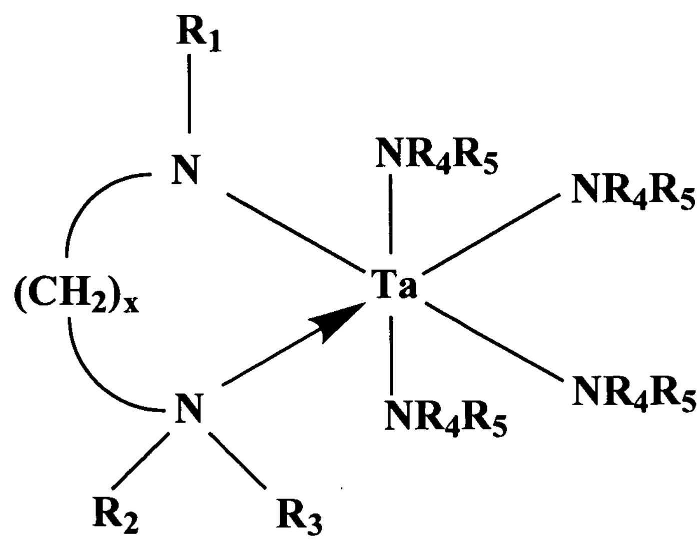
DETAILED DESCRIPTION OF THE INVENTION, AND PREFERRED EMBODIMENTS THEREOF

The present invention is based on the discovery of highly advantageous Ta and Ti source reagents, including Ta source reagents useful for forming Ta-based barrier layers on substrates such as microelectronic device structures for applications such as copper metallization of semiconductor device structures.

The Ta source reagents of the invention include TaN source reagents including Ta amides, as well as single source precursors that are advantageous for the deposition of TaSiN and TiSiN in which silicon is incorporated at the molecular level into the precursor.

In the provision of Ta amide precursors for the formation of TaN barrier layers, useful precursors include tantalum amide precursor compositions comprising at least one tantalum amide species selected from the group consisting of:

(i) tethered amine tantalum complexes of the formula:



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wherein:

X is 2 or 3;

each of R_1-R_5 is independently selected from the group consisting of H, C_1-C_4 alkyl, aryl (e.g, phenyl), C_1-C_6 perfluoroalkyl (e.g., a trifluoroalkyl substituent whose alkyl moiety is C_1-C_4 alkyl, such as trifluoromethyl), and trimethylsilyl;

(ii) β-diimines of the formula:

$$TaG_xQ_{5-x}$$

wherein:

G is a β-diimino ligand;

each Q is selected from the group consisting of H, C_1-C_6 alkyl, aryl and C_1-C_6 perfluoroalkyl; and

x is an integer from 1 to 4 inclusive;

(iii) tantalum diamide complexes of the formula

$$Ta(N(R_1)(CH_2)_xN(R_2))_y(NR_3R_4)_{5-2y}$$

wherein:

x is 1 or 2;

y is 1 or 2;

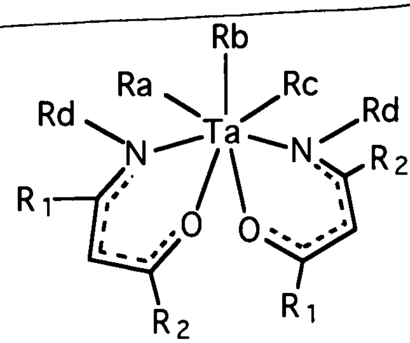
each of R_1-R_4 is independently selected from the group consisting of H, C_1-C_4 alkyl, aryl, perfluoroalkyl, and trimethylsilyl;

(iv) tantalum amide compounds of the formula

$$Ta(NRR')_5$$

wherein each R and R' is independently selected from the group consisting of H, C_1-C_4 alkyl, phenyl, perfluoroalkyl, and trimethylsilyl, subject to the proviso that in each NRR' group, $R \neq R'$;

(v) β-ketoimines of the formula



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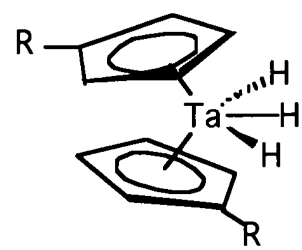
wherein each of R_1, R_2, R_a, R_b, R_c and R_d is independently selected from H, aryl, C_1-C_6 alkyl, and C_1-C_6 perfluoroalkyl; and

(vi) tantalum cyclopentadienyl compounds of the formula



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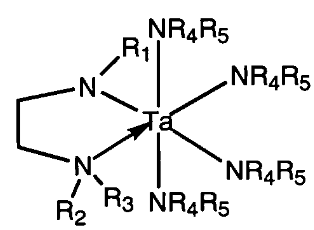
wherein each R is independently selected from the group consisting ~~of~~ H, methyl, ethyl, isopropyl, t-butyl, trimethylsilyl.

For the growth of TaN barrier layers it is desirable that the precursors be free of oxygen so that the formation of tantalum oxide is avoided. Tantalum amides, which have preexisting Ta-N bonds, are therefore attractive precursors. However, homoleptic tantalum amides such as $Ta(NMe_2)_5$ suffer from reduced volatility, due to the bridging of

multiple metal centers through the $-NMe_2$ group, analogous to that observed for $Ta(OEt)_5$.

The present invention enhances the volatility of tantalum amides by limiting the degree of intermolecular interactions. To thwart such interactions the use of tethered amine ligands may be employed. For instance, substitution of one of the -NMe2 groups with $-N(CH_3)(CH_2CH_2)-NMe_2$ gives the tantalum amide composition of formula **I** below, a monomer, with a stable five-membered metallacycle structure. A variety of tethered ligands may be similarly employed. Ligand species of the general formula $R_1N(CH_2)_xNR_2R_3$ where R_1, R_2, R_3 can be independently chosen from H, Me, Et, ${}^tBu$, Ph, ${}^iPr$, CF_3 or $SiMe_3$ groups, appropriately selected to maximize volatility, are preferred. X can be 2 or 3 so that stable 5 or 6 membered chelating rings result.



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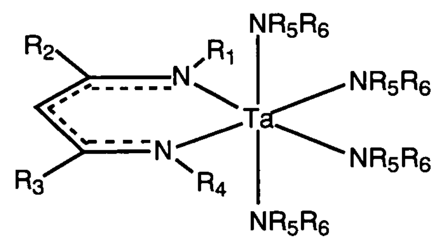
I

The use of ß-diimmines offers alternative precursor compositions that maximize volatility and minimize detrimental exchange reactions. For instance, $Ta(nacnac)(NMe_2)_4$

(directly analogous to $Ta(OiPr)_5(thd)$) is illustrative of precursors of such type that may be usefully employed for the deposition of TaN diffusion barriers. In complexes of the formula $Ta(R_1N\text{-}C(R_2)\text{-}CH\text{-}C(R_3)\text{-}N(R_4))_x(NR_5R_6)_{5-x}$, formula (**II**) below, R_1 - R_6 can each be independently selected from substituent species such as H, Me, Et, ^{t}Bu, Ph, ^{i}Pr, $SiMe_3$, and CF_3.



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II

Alternatively, the TaN precursor may utilize diamide ligands such as $N(R_1)(CH_2)_xN(R_2)$ to form mixed ligand complexes such as those of the formula $Ta(N(R_1)(CH_2)_xN(R_2))_x(NR_3R_4)_{5-2x}$, formula (**III**) below, in which each of R_1-R_4 can be independently selected from substituents such as H, Me, Et, ^{t}Bu, Ph, ^{i}Pr, $SiMe_3$, and CF_3 groups.

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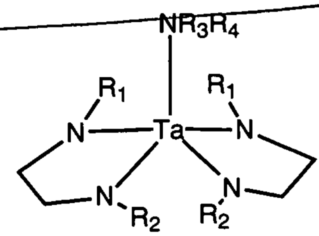

III

In a simple form, unsymmetrical amides can be employed to thwart intermolecular interactions and disrupt crystal packing forces. Thus, a suitable precursor could be $Ta(NRR')_5$ where R and R' can be any combination of H, Me, Et, ^tBu, Ph, ^iPr, $SiMe_3$, CF_3, Ph, Cy but R≠R'. As used herein, the term Ph denotes phenyl, and Cy denotes cycloalkyl.

The aforementioned precursors of the present invention provide Ta source reagents that have beneficial volatility characteristics for applications such as chemical vapor deposition, and are easily and economically synthesized. The Ta source reagents

a of the invention ~~utilized~~ utilize molecular geometries that are controlled by subtle steric effects.

As an example of such subtle steric effects, $Ta(NMe_2)_5$ reportedly possesses a square pyramidal structure and therefore possess a vacant coordination site useful for coordination to other metal centers via a bridging $-NMe_2$ group, analogous to that observed for $Ta(OEt)_5$. $Ta(NMe_2)_5$ therefore is a solid and suffers from reduced

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volatility. Increasing the steric bulk of the ligand by replacement of the $-NMe_2$ by $-NEt_2$ results in a trigonal bipyramidal compound, $Ta(NEt_2)_5$, due to the increased steric bulk of the ethyl group compared to the methyl groups in $Ta(NMe_2)_5$. Since trigonal bipyramidal compounds have no free coordination site $Ta(NEt_2)_5$ is a liquid but it is unstable to heat.

In order to enhance the volatility of the complex by altering the geometry around the metal center to trigonal bipyramidal, without adding undue steric bulk, $Ta(NMeEt)_5$ was synthesized. $Ta(NMeEt)_5$ is:

(i) a liquid.

(ii) more volatile than $Ta(NMe_2)_5$ or $Ta(NEt)(NEt_2)_3$ (see Fig. 1).

(iii) stable to heat up to its boiling temperature (see Fig. 2).

These properties make $Ta(NMeEt)_5$ a highly desirable precursor for CVD that is superior to the prior art, as shown in Figure 1, which is a thermal gravimetric analysis (TGA) plot comparing the volatility of $Ta(NMeEt)_5$ vs. $Ta(NEt)(NEt_2)_3$ and $Ta(NMe)_5$.

Figure 2 shows an STA plot of $Ta(NMeEt)_5$. Note there is no event in the differential scanning calorimetry (DSC) curve prior to boiling, indicating stability to decomposition.

Figure 3 shows an ^{1}H and ^{13}C NMR plot of $Ta(NMeEt)_5$ showing five equivalent amide groups.

In the Ta amide precursors of the invention, the Ta substituents preferably include substituents having slightly increased steric size than $-NMe_2$. Such Ta amide precursors include compounds of the general formula $Ta(NR_1R_2)_5$, wherein R_1 and R_2 are independently selected from substituents such as -H, -Me, -Et, $-CH_2CH(Me)-$, $-CF_3$, -^{t}Bu, -^{i}Pr, and $SiMe_3$.

In the broad practice of the present invention, other compounds of the general formula $Ta(NR_1R_2)_3(NR_2R_3)_2$ can also be optimized for volatility and stability. In such precursor compositions, the steric size of $-NR_1R_2 > -NR_2R_3$ so that the more bulky $-NR_1R_2$ group occupies the axial position and the $-NR_2R_3$ group occupies the more sterically crowded equatorial position. In these compositions, R_{1-4} can be selected from any combination of -H, -Me, -Et, $-CH_2CH(Me)-$, $-CF_3$, -^{t}Bu, -^{i}Pr, and $-SiMe_3$.

The deposition of Ta metal in accordance with the process of the present invention may be carried out with a wide variety of precursor materials of the types disclosed herein. In some cases, it may be detrimental to have an oxygen containing ligand present in the molecule which could ultimately result in Ta_2O_3 formation. In such

instances, the use of ß-ketoimine or ß-diimine ligands, such as those described below, enables highly efficient chemical vapor deposition of TaN and Ta metal.

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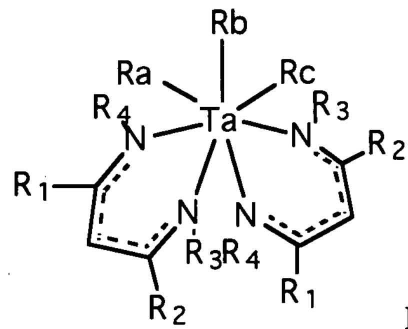

I

In compound **I,** R_1, R_2, R_3 and R_4 may be alike or different and are independently selected from substituents such as H, aryl, C_1 - C_6 alkyl, and C_1 - C_6 perfluoroakyl. In a specific embodiment, R_3 will most likely be H, aryl, C_1 - C_6 alkyl, or C_1 - C_6 perfluoroalkyl. Alternatively, R_1 or R_2 may be identical to R_3. R_a, R_b, and R_c may be alike or different and are independently selected from the group consisting of H, aryl, C_1 - C_6 alkyl, or C_1 - C_6 perfluoroalkyl.

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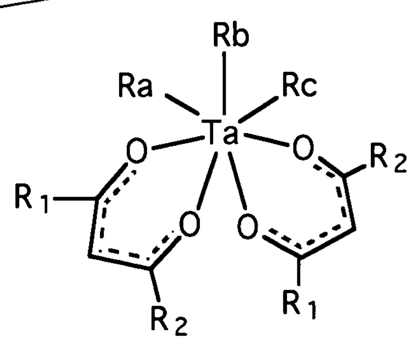

II

In compound **II**, R_1 and R_2 may have the same restrictions as discussed above for compound **I**. R_a, R_b, and R_c, may be equal or different and can be H, aryl, perfluoroaryl, C_1 - C_6 alkyl, or C_1 - C_6 perfluoroalkyl.

Various trimethyl tantalum bis(ß-diketonate) complexes may be employed as useful Ta precursors in the broad practice of the invention. For example, $Me_3Ta(acac)_2$ has a melting point of 83 °C, $Me_3Ta(tfac)_2$ has a melting point of 107 °C and $Me_3Ta(hfac)_2$ has a melting point of 109 °C. The volatility generally increases in the same order with increasing fluorine substitution. These types of materials are potentially usefully employed for Ta film growth in the presence of hydrogen, forming gas or other reducing species. They may also be usefully employed for oxide formation, as for example in CVD of $SrBi_2Ta_2O_9$.

A third class of materials that is potentially usefully employed for the deposition of Ta metal or TaN films has a hydride precursor structure, as depicted in compound **III** below. Such compositions have not previously been used for Ta or TaN film growth.

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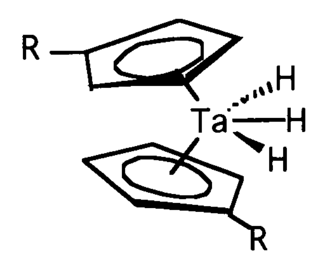

III Bis (cyclopentadienyl) tantalum (V) trihydride

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The structure of this Ta precursor may be altered to enhance thermal stability, volatility or physical properties and to achieve the desired film properties, namely high purity and low resistivity. Potential substituents where R on the cyclopentadienyl moiety is varied include R=H, Me, Et, i-Pr, t-Bu, TMSi, etc. in which the substituent is selected to modify the precursor properties. This general class of materials is well-suited for Ta film growth especially in the presence of H_2 or forming gas.

In use, the precursors of the invention may be employed in a neat liquid form, or alternatively they may be utilized in solution or suspension form, in which the precursor is mixed, blended or suspended in a compatible liquid solvent such as a solvent composition of the type disclosed in U.S. Application Serial No. 08/414,504 filed March 31, 1995, in the names of Robin A. Gardiner, Peter S. Kirlin, Thomas H. Baum, Douglas Gordon, Timothy E. Glassman, Sofia Pombrik, and Brian A. Vaartstra, the disclosure of which is hereby incorporated herein by reference in its entirety.

The solvent may for example be selected from the group consisting of C_6-C_{10} alkanes, C_6-C_{10} aromatics, and compatible mixtures thereof. Illustrative alkane species include hexane, heptane, octane, nonane and decane. Preferred alkane solvent species include C_8 and C_{10} alkanes. Preferred aromatic solvent species include toluene and xylene.

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The present invention also contemplates various single source precursors for the formation of TaSiN and TiSiN layers on substrates. Two general variant approaches can be used for the provision of single source precursors that are advantageous for the deposition of TaSiN and TiSiN. These approaches are:

(1) use of silyl amides as precursors; and

(2) provision of direct metal-silicon bonds in the precursors.

Metal silylamides represent the most direct and cost-effective method for the introduction of silicon into the product film formed by the precursor. Examples include the clean formation of $Bi_{12}SiO_{20}$ upon heating $Bi(NSiMe_3)_3$ in oxygen. For the deposition of TaSiN and TiSiN suitable precursors include those of the general formula:

$Ta(NR_1R_2)_x(NR_3R_4)_{5-x}$ / $Ti(NR_1R_2)_x(NR_3R_4)_{4-x}$

or

$Ta(NR_1)(NR_2R_3)_3$

where each of R_1, R_2, R_3 and R_4 are independently selected from the group consisting of H, C_1-C_8 alkyl (e.g., Me, Et, ^tBu, ^iPr, etc.), aryl (e.g., phenyl), C_1-C_8 perfluoroalkyl (e.g., CF_3 or a fluoroalkyl whose alkyl moiety is C_1-C_4, such as trifluoromethyl), or a silicon-containing group such as silane (SiH_3), alkylsilane, (e.g., $SiMe_3$, $Si(Et)_3$, $Si(^iPr)_3$,

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$Si(^tBu)_3$, perfluoroalkylsilyl (e.g., $Si(CF_3)_3$), triarylsilane (e.g,, $Si(Ph)_3$), or alkylsilylsilane (e.g., $Si(SiMe_3)_x(Me)_{3-x}$). The number of silicon-containing R groups can be used as an independent variable to control the amount of silicon in the film. For precursors of the type $Ta(NR_1)(NR_2R_3)_3$ the location of the R group (i.e., imide vs. amide) will also determine the incorporation efficiency of silicon into the film.

Precursors containing preexisting metal to silicon bonds are potentially highly effective for the deposition of TaSiN/TiSiN. Useful precursors have the general formula:

$Ta(SiR_1R_2R_3)_x(NR_4R_5)_{5-x}$ / $Ti(SiR_1R_2R_3)_x(NR_4R_5)_{4-x}$

where R_{1-5} can any be combination of H, Me, Et, ^tBu, Ph, ^iPr, CF_3, SiH_3, $SiMe_3$, $Si(CF_3)_3$, $Si(Et)_3$, $Si(^iPr)_3$, $Si(^tBu)_3$, $Si(Ph)_3$, $Si(SiMe_3)_x(Me)_{3-x}$. Two illustrative titanium amides with metal to silicon bonds are $Ti(Si(SiMe_3)_3)(NMe_2)_3$ and $Ti(Si(SiMe_3)_3)(NEt_2)_3$.

Another class of useful precursors are complexes where one of the amide or silyl groups has been replaced by a cyclopentadiene or substituted cyclopentadiene. These precursors have the general formula;

$(Cp^n)Ta(SiR_1R_2R_3)_x(NR_4R_5)_{4-x}$ / $(Cp^n)_2Ti(SiR_1R_2R_3)(NR_4R_5)$

where, once again, R_{1-5} can any be combination of H, Me, Et, ^tBu, Ph, ^iPr, CF_3, SiH_3, $SiMe_3$, $Si(CF_3)_3$, $Si(Et)_3$, $Si(^iPr)_3$, $Si(^tBu)_3$, $Si(Ph)_3$, $Si(SiMe_3)_x(Me)_{3-x}$ and Cp^n is $C_5H_xMe_{(5-x)}$ (where x = 0-5). Cyclopentadienyl complexes of Ta and Ti containing direct metal to silicon bonds have not heretofore been used or considered for formation of TaN, TiN, TaSiN or TiSiN films.

For liquid delivery CVD of Ta- or Ti-based films or coatings on a substrate, the corresponding source reagent may be provided as a liquid starting material which then is vaporized to form the precursor vapor for the chemical vapor deposition process.

The vaporization may be carried out by injection of the liquid in fine jet, mist or droplet form into a hot zone at an appropriate temperature for vaporization of the source reagent liquid. Such injection may be carried out with a nebulization or atomization apparatus of conventional character, producing a dispersion of finely divided liquid particles, e.g., sub-micron to millimeter diameter scale. The dispersed liquid particles may be directed at a substrate at a sufficiently high temperature to decompose the source reagent and produce a coating of the Ta- or Ti-based material product on the substrate.

Alternatively, the liquid may be dispensed from a suitable supply vessel of same, onto a heated element, such as a screen, grid or other porous or foraminous structure, which is heated to a sufficiently high temperature to cause the liquid to flash volatilize into the vapor phase, as for example in the manner described in U.S. Patent 5,204,314 to

Peter S. Kirlin, et al. and U.S. Patent 5,711,816 to Peter S. Kirlin, et al., the disclosures of which hereby are incorporated herein by reference in their entirety.

Regardless of the manner of volatilization of the source reagent, the vapor thereof is flowed to contact the substrate on which the Ta-based or Ti-based material is to be deposited, at appropriate deposition conditions therefor, which may be readily determined within the skill of the art, by the expedient of varying the process conditions (temperature, pressure, flow rate, etc.) and assessing the character and suitability of the resulting deposited material.

As an alternative to the use of the source reagent in a neat liquid form, the source reagent may be dissolved or mixed into a compatible solvent medium which does not preclude the efficacy of the resulting composition for CVD usage. For example, the source reagent may be utilized in a solvent composition of the type disclosed in the aforementioned U.S. Application Serial No. 08/414,504 filed March 31, 1995, in the names of Robin A. Gardiner, et al. The resulting solution or suspension of the source reagent and solvent medium may then be injected, dispersed, flash vaporized, or otherwise volatilized in any suitable manner, as for example by the techniques described above in connection with the use of the neat liquid source reagent.

While the invention has been described illustratively herein with respect to specific features, aspects and embodiments thereof, it is to be appreciated that the utility

of the invention is not thus limited, but rather extends to and encompasses other applications, aspects, features and embodiments, such as will readily suggest themselves to those of ordinary skill in the art. The invention is therefore to be broadly construed and interpreted, in reference to the ensuing claims.